



Interactive comment on “Organic particle types by single-particle measurements using a time-of-flight aerosol mass spectrometer coupled with a light scattering module” by S. Liu et al.

Anonymous Referee #1

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This paper presents an analysis of single particle mass spectra collected using the LS-ToF-AMS, consisting of an improved light scattering module integrated with the Aerodyne ToF-AMS. The authors discuss hardware improvements, their impact on instrument performance, estimates of instrument collection efficiency, and identification/classification of particle types based on organic mass spectra. The technique and resulting dataset are novel and of great interest. However, some major issues exist within the data analysis and a number of conclusions are not well supported by the data. First, the collection efficiency analysis depends on correct identification of LS-detected particles that produce/do not produce a detectable mass spectrum. The cur-

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rent method is not valid across the entire size range to which it is applied (see Comment 16). Second, there are a number of flaws in the identification of Clusters II and III with specific sources and processes, and especially in their relation with ensemble-derived factors (see Comments 19-25). These issues are fundamental to the conclusions of the paper and major revisions are required before this manuscript can be published. Detailed comments are provided below.

Major Comments

1. P3049 L14-16: “The single particle mode in the ToF-AMS operation is typically turned off during field measurements to conserve data storage and processing time.” The authors are referring to the so-called “brute force single particle (BFSP)” mode, where the AMS saves either (1) all MS extractions within a chopper cycle, with the fraction of cycles saved limited by the data transfer rate, or (2) all MS extractions within a chopper cycle, with the chopper cycles selected based on a user-set chemical profile (e.g. all particles with nitrate-containing peaks above a set threshold). This mode is distinct from the LS-based triggering discussed later in the paragraph, and the difference should be noted explicitly.

2. P3051 L18-21: “The detection process is fast enough (~ 100 us), compared to the traveling time (~ 5 ms) of the particles in the particle-sizing chamber, to allow correlated measurements of single particle light scattering and chemical compositions.” This could be phrased more clearly. I am not sure what is meant by “detection process.” It appears to be the collection time for a single mass spectrum (i.e. single extraction), but it is not clear whether vaporization and ion flight times are included. I’m also not clear why the relationship between “detection process” and particle flight time determines whether correlated LS/chemical composition measurements are possible. Shouldn’t the chopper frequency also play a role, as the combination of chopper frequency and spread in particle flight times governs the probability of coincident particles at the LS unit?

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3. P3051 L23-26: “By measuring particle flight time between the mechanical chopper and the light scattering laser and thermal vaporizer, particle vacuum aerodynamic diameter (dva) can be determined from a calibration curve, which relates particle flight time to particle size for atomized ammonium nitrate particles of known sizes.” This are several issues with this statement. (1) The dva calibration relates particle velocity (i.e. flight time over a known distance; not simply flight time) to dva. This is a useful distinction to make, as it clarifies that dva can be extracted from flight time measurements of chopper-to-vaporizer, chopper-to-LS, or LS-to-vaporizer, which is slightly unclear in the original statement. (2) The dva calibration applies for ALL particles, not simply ammonium nitrate. I am not sure whether the authors intended to imply this, but the current phrasing is ambiguous. (3) Does the reference to ammonium nitrate indicate that the dva calibration was performed using DMA-selected ammonium nitrate? In this case, the method and accuracy of the DMA size calibration should be discussed. The calibrations must be somehow referenced to a primary size standard such as PSL spheres.

4. P3051 L 27-30: “The density (1.4 g cm⁻³) was derived by comparing AMS-measured mass size distribution with DMA-measured volume size distribution detailed in Lars et al. (2012).” This seems an unnecessarily crude method of estimating dg, and several parallel methods are possible using the system in this paper. Cross et al. (2007) demonstrated the LS-ToF-AMS to provide direct estimates of dg from the optical scattering signal. This approach seems ideal for the current manuscript; why is it not used? The AMS ensemble measurements can also be used to estimate particle density based on the composition of the individual components and assumed densities for these components. Finally, it is not clear how much variation was observed in the analysis of Lars et al. or how this analysis was performed. Unfortunately, Lars et al. (2012) does not appear in the reference list. A minor point is that the DMA does not count particles; the instrument used for this should be reported.

5. The advantages of the new comparator circuit are not clearly described (P3052 L10-

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17). The authors need to be careful with their terminology regarding data transfer vs. data saving. Without the comparator circuit, the LS data for every chopper cycle must be transferred to the computer where a software evaluation is conducted to determine whether a particle is present. This transfer process is longer than an individual chopper cycle, thereby reducing LS sampling efficiency. In the new system, this evaluation is conducted by the comparator circuit, removing the need for data transfer during blank chopper cycles. LS and MS data are now transferred to the computer and saved only for particle-containing chopper cycles, greatly increasing the instrument duty cycle. An additional improvement, which is not currently mentioned, is the implementation of the GZIP compression algorithm for the single particle data files. This reduces file size, thereby reducing data transfer time and improving the duty cycle.

6. The “light scattering particle counter” (P3052 L18-26) is part of the comparator circuit discussed above, and I suggest these two discussions be combined.

7. The authors note the dependence of the duty cycle on particle concentration (P3053 L2-7), which is very welcome. If the data are available, it would be very useful to provide a plot of this dependence in the supplement, given this is the first published characterization of the comparator circuit-based LS system.

8. P3053 L21-22: What is meant by “summed light scattering signals” (also applies to Fig. 1). Is this the time-integrated light scattering signal?

9. P3053 L23-25: Two separate criteria are given for determining the detection limit (optical signal and chemical ion signal). Which of these two is typically the limiting factor, or do they present similar restrictions?

10. Fig. 1a shows that the population of organic-dominated particles tends toward lower sizes relative to the total ensemble. It appears that these particles coincide predominantly with Cluster III (Fig. 1b). The authors suggest that this is a result of these particles being primary and nonspherical, with the nonspherical particles containing black carbon. The assumption of primary particles is plausible based on the

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mass spectrum (Fig. 3a-iii), as it resembles hydrocarbon-like and cooking OA spectra published in numerous other studies. However, the authors compare it to a mass-weighted average of cooking OA, petroleum SOA, and traffic/biogenic nighttime OA, which would imply a strong secondary component. This contradicts the assertion of a primary aerosol. Regarding the suggestion of black carbon-containing nonspherical particles, the BC inclusion would have to be quite significant to affect the particle shape. It seems unlikely that such particles would occur so frequently in the 300–600 nm dgeo range. Perhaps this could be explored by comparing the measured ion signal vs. the theoretical signal from a particle with this size (i.e. looking for discrepancies in mass balance due to the BC core). However, it is possible that current estimate of dgeo is too uncertain for this. Another possibility is simply that the authors' assumption of a uniform density (see comment 4) is inadequate. It is quite likely that organic-dominated particles will have lower densities. Thus the estimate of dgeo (the quantity most closely related to LS signal) may be biased low for such particles. Finally, note that on P3054 L13, “diameter” should be “dva.” It should also be noted here that, if the authors' assumption of non-spherical particles is correct (or the particle density is lower as suggested above), the estimate of dgeo will be biased low.

11. Another curious feature of Fig. 1a is that the organic-dominated particles yield higher LS signals than the other particles. Y-axis values for organic-dominated particles with dgeo > ~325 nm are almost universally > 5, while the other particles virtually never cross this threshold. Do the authors have an explanation for this? As a follow-up to Comment 10, note that nonspherical particles will have a broader particle beam than spherical particles of the same dva. This will tend to lead to lower-intensity LS signals, because a larger fraction of particles intersects the laser beam at lower laser intensities. This is contrary to the observed behavior, and further suggests nonsphericity/BC inclusion is unlikely.

12. P3054 L14: This should be “overall duty cycle” not “overall chopper duty cycle.” The duty cycle under discussion contains but is not limited to the chopper duty cycle,

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as discussed correctly later in the paragraph. Is the saving duty cycle calculated as a function of time, or is the single value of 0.62 applied to the entire study? It seems to be the second, but it should be the first. The authors have previously noted the saving duty cycle dependence on particle concentrations, so a constant value is probably not warranted.

13. P3054 L23: It is not clear to me that the first two reasons for decreasing detection efficiencies for small particles are different (i.e. broadening of the particle beam beyond the particle/laser overlap vs. low intensities for small particles at the laser edges). Because the laser edges are not a step function, these two issues are linked and should probably be discussed together. Have the authors measured the relative importance of laser/particle overlap vs. laser size detection limit? This can be done easily by measuring LS detection efficiency as a function of aerodynamic lens position, with the lens walked across the laser (similar to the standard lens alignment procedure).

14. The agreement between the LS-AMS and DMA-measured number concentrations for particles > 400 nm dva (P3054 L25-30) is strange in light of Fig. 2, which shows an LS detection efficiency of well below 50% for dva = 400 nm. While unit detection efficiency is seen for particles of 500-700 nm dva, Fig. 2 shows that the 400-500 nm region contains on the order of 50% of the total particle concentration. (Although it is a minor fraction of the total, LS detection efficiency also decreases for dva > 700 nm). Therefore the reported slope of 1.0 should not be obtained.

15. P3055 L 24: "After comparing the physical signal identifying particle arrival (time to detector calculated from the time of light scattering, T_LS) to the chemical signal identifying particle arrival (time of mass spectrum, T_MS), each single particle was classified into one of three discrete particle types:" This is not clearly written. (1) "Arrival time" is ambiguous (this refers to T_MS, time from chopper opening (or midpoint of chopper opening?) to peak of the mass intensity profile, but is easily confused with particle arrival time at the vaporizer. (As a side note, is the ion transit time from vaporizer to detector estimated, or is this assumed to be negligible?) (2) There is no "physical sig-

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nal” measured. Instead the predicted T_{MS} , calculated from particle velocity (chopper opening/midpoint to laser) and chopper-to-vaporizer distance (perhaps plus ion transit time) is compared to the measured T_{MS} . (3) Is TLS the time from chopper opening/midpoint to laser or the “predicted T_{MS} described in this comment? It seems the latter is meant, but the authors’ definition (“time to detector calculated from the time of light scattering, T_{LS} ”) is not clear, though somewhat suggesting the former.

16. There is a serious issue with the identification of null particle events (P3056). The 100-ion threshold used to distinguish null vs. prompt/delayed is greater than the expected number of ions for particles with d_{geo} extending well into the measured size range. Consider a 300 nm spherical particle with the effective density and molecular weight of ammonium nitrate, and the ionization efficiency of nitrate. Nitrate ionization efficiencies (IEs) for the HR-ToF-AMS are typically in the range of 10^{-8} to 10^{-7} ions/molecule. The 300 nm particle in question would yield 19, 93, and 185 ions, for IEs of 1×10^{-8} , 5×10^{-8} , and 1×10^{-7} , respectively. Put another way, for these IEs one would only expect to measure more than 100 ions for particles larger than 527, 308, or 245 nm (d_{geo}). The exact cutoff of course depends on the IE of the instrument used for this study, but it is very unlikely that this bias can be ignored. Note that the Cross et al. (2009) study to which the present results are compared utilized a C-ToF-AMS, which has a much higher IE and is therefore unlikely to be affected by this issue. Note that the estimated ions per particle discussed above assumed the molecular weight of nitrate. Particles dominated by higher molecular weight species (e.g. sulfate, organics) will contain fewer molecules, generate fewer ions, and be more strongly affected by this bias. Before the collection efficiency results can be evaluated, the authors must thoroughly address the implications of the 100-ion cutpoint.

17. The differences in number vs. mass-based CE (P3056 L17) may also be due to the 100-ion cutpoint issue discussed above. It may also be due to problems in the AMS/DMA comparison, particularly if the constant density of 1.4 g cm^{-3} is used. See Ahlm et al. 2012. It also seems unlikely that there is sufficient mass below 180 nm d_{va}

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to account for the increase in mass-based CE (0.8) relative to number-based CE (0.5). Even if much of the mass is found in small particles, the decrease in AMS transmission efficiency for particles with $d_{va} < 100$ nm would prevent such an increase. The authors can demonstrate that their hypothesis is plausible through analysis of AMS and DMA size distributions. Otherwise, this explanation should be removed.

18. The attribution of decreased CE in the 800-1000 nm d_{va} size range to dust (P3056 L22-24) seems quite speculative. It is possible that larger particles are inherently more difficult to vaporize. Have the authors tested this, e.g. with ammonium sulfate? Or perhaps there are size-dependent chemical differences (e.g. enhanced sulfate) that contribute to a lower CE? This would be somewhat consistent with Fig. 1a, where the high-CE organic-dominated particles are not present at large sizes.

19. P3059 L 14-18: “The number concentration of Cluster II particles increased at night, likely resulting from temperature-driven condensation of this particle type under low-temperature conditions. . .” It is likely that condensation of Cluster II-like material, rather than condensation of new Cluster II particles, is the driving factor (this is probably just a phrasing problem). But this also strongly suggests a gradient between Cluster II and the other clusters, despite the metrics for assessing gradients discussed on the previous page. It is worthwhile for the authors to take a closer look at the temperature-dependent evolution of mixing state. How are particles classified in transitional periods when Cluster II-like material is partially condensed?

20. Further to Comment 19, the identification of Cluster II as semivolatile material is questionable. The authors argue that the increase in number concentration of Cluster II particles overnight (i.e. lower temperature) implies semivolatile material. However, Fig. 7 indicates that all three clusters follow approximately the same diurnal pattern. It is possible there are differences in the time series that are not visible in this figure; in this case the actual number concentration time series diurnal patterns should be added. It would also be beneficial to show these time series for the entire campaign, and not just the diurnal patterns.

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21. P3059 L18-20: “m/z 29 and 57 are markers for HOA and m/z 27, 41, 55, and 69 are cooking organic aerosol (COA) tracers.” This is overstated. As shown in a number of studies, these 6 peaks contribute strongly to both HOA and COA, although they trend in the direction stated. A characteristic time series and/or diurnal cycle is really required to identify the contribution of either. Given that both the suspected sources are primary, one would expect the particles to be externally mixed. Therefore it should be possible to distinguish HOA and COA through a more detailed analysis. One approach would be to investigate evolution of the frequency distribution of m/z 55/57 ratios for Cluster III particles as a function of time of day. If the particles are in fact an external HOA/COA mixture, then differences should be evident.

22. P3059 L25 to P3060 L2: Correlation with C₄H₉⁺ alone is insufficient to postulate HOA-dominated particles. At a minimum, m/z 55 and 57 should be compared within this subset to see if they are more HOA-like than the entire Cluster III. The argument for nonspherical particles is presently not convincing, as discussed in Comments 10 and 11.

23. The identification of Cluster II with semivolatiles (see Comments 19 and 20) is made more questionable by Fig. 8. The mass fraction of this cluster does not increase during the night when temperatures are lower. If anything, the mass fraction is higher during the day. How does this fit with the interpretation of Cluster II?

24. Section 3.3. The mass spectral comparison between ensemble and single particle factors supports the authors’ interpretation, although the Cluster II spectrum is quite interesting. The fraction of m/z 43 is extremely high; I cannot remember seeing a similar SV-OOA spectrum. Do the authors have any thoughts on why this spectrum might be so unique?

25. Section 3.3. In Fig. 8, the agreement between the cluster and the low O/C alkane SOA + low O/C aromatic SOA is quite poor as is the COA+PO SOA+NOA vs. Cluster III correlation. This figure does not provide evidence for a connection between the

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ensemble and single particle factors for either case. In fact, the agreement of Cluster II vs. COA+PO SOA+NOA and Cluster III vs. low O/C alkane SOA + low O/C aromatic SOA looks much better. Unless the cluster or ensemble traces are reversed in the figure, this very much calls into question the associations suggested by the authors. These contradictions should be addressed in Section 3.3. They must be resolved satisfactorily for Clusters II and III to be related to the ensemble factors. Otherwise this conclusion should be removed and the section rewritten accordingly.

26. Mass spectra and time series for the minor clusters (P3061 L10-11) should be shown, perhaps in the Supplement.

27. (Section 4: Concluding remarks): There are a number of issues with this section, related to the comments above. Specific issues are: (1) the prompt vs. null classification (P3061 L18-19, see Comment 16); (2) estimate of number-based CE for $d_{\text{p}} > 100$ nm (P3061 L23-24, see Comment 16); (3) explanation for discrepancies between mass- and number-based CE (P3061 L 24-26, see Comment 17); (4) identification of cluster sources (P3062 L5-7, see Comments 19-25); (5) agreement between ensemble and single particle factors (P3062 L10-12, see Comment 25).

Minor Comments

P3049 L14: “chopper cycle (143-Hz frequency).” This frequency is set by the operator and can vary considerably. For the Introduction, it is better to note the typical range of values.

P3050 L13: Should give the version number and author for Sparrow (D. Sueper, U. of Colorado-Boulder). Version is given later (P3053 L19) but should be here instead.

P3051 L7: Should this be 120, 120 and 60s? Otherwise the values don’t add up to 5 min.

P3051 L12: “. . . are focused by a series of aerodynamic lenses. . .” Technically, this unit is a single aerodynamic lens that consists of a converging series of apertures.

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P3051 L17: Suggest replacing “detector” with “mass spectrometer.” “Detector” is frequently taken to mean the MCP.

P3051 L 29-30: “distribution” should be “distributions” (occurs twice).

P3052 L9-10: “. . .the chopper frequency is the fundamental clock for all ToF-AMS data acquisition.” This is true only in the PToF or LS modes.

P3052 L11: “presences” should be “presence.”

P3054 L11: “dominating” should be “dominated.”

P3054 L27: “similar result” should be “a similar result.”

P3055 L17: “nitrate and sulfate.” The m/z list would also include ammonium signals (m/z 15).

P3055 L27: “into” should be “as.”

P3059 L26: “mass concentration” should be “the mass concentration.”

P3059 L27: “correlated to” should be “correlated with.”

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